Insertion of a Water Oxygen Atom into a Phosphorus−Metal Bond: From a P-Coordinated (Diphenylphosphino)alkyne to a Coordinated η^2(*O*,*C*)-Vinyldiphenylphosphine Oxide[†]

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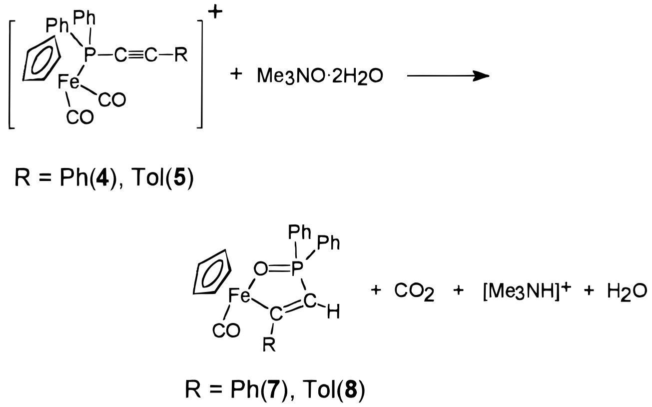
Summary: The reaction of $[(\mathrm{Fp})\mathrm{Ph_2PC{\equiv}CR}][\mathrm{BF_4}]$ *(Fp* = $(\mathrm{C_5H_5})\mathrm{Fe(CO)_2}$*; R* = *H (**1**), Me (**2**), tBu (**3**), Ph (**4**), Tol (**5**)) with* $(\mathrm{CH_3})_3\mathrm{NO{\cdot}2H_2O}$ *(**6**) was studied, and the new complexes* $[\mathrm{CpFe(CO)}(\eta^2(O,C)\text{-}\mathrm{Ph_2P(O)CH{=}CR})]$ *(R* = *Ph (**7**), Tol (**8**)) were isolated. Compound **8** was characterized by X-ray diffraction. An isotopic labeling study showed that the oxygen atom bonded to phosphorus came from a water molecule.*

Reactions involving oxidation of phosphines are important steps in chemistry because of their relevance to enzymatic systems and catalytic oxidation processes.[1] The mechanistic aspects of these reactions have been studied by different approaches such as isotopic labeling and kinetic and spectroscopic methods.[2] We report here on the surprising oxidative conversion of a cationic iron P-coordinated (diphenylphosphino)alkyne to an iron vinyldiphenylphosphine oxide. We have previously reported the synthesis of the family of cationic complexes $[(\mathrm{Fp})\mathrm{Ph_2PC{\equiv}CR}][\mathrm{BF_4}]$ (Fp = $(\mathrm{C_5H_5})\mathrm{Fe(CO)_2}$; R = H (**1**), Me (**2**), *t*Bu (**3**), Ph (**4**), Tol (**5**)), in which significant π C≡C bond polarization has been suggested.[3] To examine the possibility of an intramolecular reaction between the polarized alkyne and the iron atom, the reactivity of such complexes with trimethylamine *N*-oxide dihydrate ($(\mathrm{CH_3})_3\mathrm{NO{\cdot}2H_2O}$; **6**) has been studied. The reaction of $(\mathrm{CH_3})_3\mathrm{NO}$ with a metal carbonyl oxidizes the CO ligand so that an unsaturated organometallic moiety is generated,[4] which can react with the alkyne ligand. Complexes **1**−**5** react rapidly with **6** in dichloromethane under ambient conditions and in a stoichiometric ratio to provide green solutions, which lead to different results according to the nature of the R groups. The reaction of complexes **1**−**3** gave solutions from which pure products could not be isolated. However, when R is an aryl group (**4** and **5**), after extraction with hexane, green crystalline solids of complexes **7** and **8** were obtained in high yields (Scheme 1).

Scheme 1



Because their spectroscopic parameters and solubility in hexane are comparable, a similar nonionic structure is suggested for both complexes. In the IR spectra only one ν(C≡O) band is present and the ν(C≡C) band is absent. Therefore, one carbonyl group has been oxidized and the alkyne is involved in the reaction. The NMR spectra show two remarkable features, a ^{31}P significant downfield shift for complexes **7** and **8** (δ 72.2 ppm) with respect to complexes **4** (δ 46.7 ppm) and **5** (δ 42.4 ppm) and a characteristic doublet (δ 6.42 ppm; J(P,H) = 48 Hz (**7**), J(P,H) = 47.2 Hz (**8**)) in the ^{1}H NMR spectra. All these results are consistent with the formation of a vinyl complex and indicate substantial modifications around the phosphorus atom. The crystal structure of complex **8** confirms the presence of a vinyl fragment as an η^2(*C*,*O*)-vinyldiphenylphosphine oxide ligand coordinated to the $(\mathrm{C_5H_5})\mathrm{Fe(CO)}$ fragment (Figure 1). The most relevant feature of this structure is the presence of the nearly planar (±0.1 Å) metallacycle $\mathrm{FeOPC_2}$. A few examples of related metallacycles have been reported with rhodium,[5] tungsten,[6] and osmium,[7] but as far as we know, this is the first iron example.

[†] Dedicated to Professor Heribert Barrera on the occasion of his 80th birthday.

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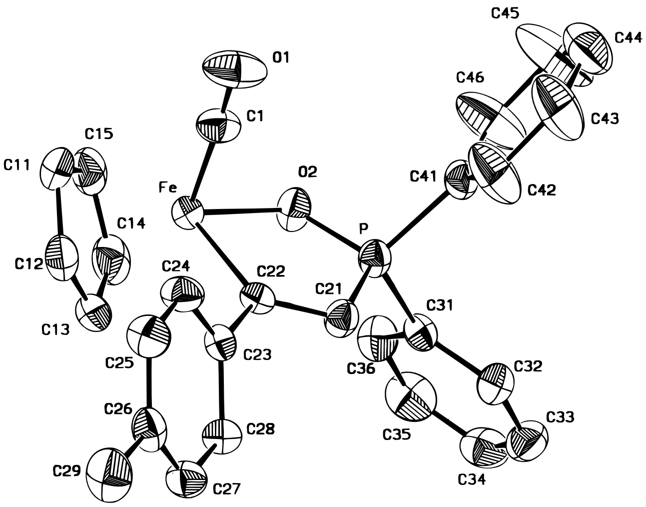

Figure 1. ORTEP drawing[8] (30% probability level) of **8** with the atomic numbering scheme.

Once the structure of the reaction product has been established, an intriguing question emerges: Where does the oxygen atom bonded to phosphorus come from? Compound **6** is a mild oxidizing agent,[9] and reactions involving oxygen transfer from nitrogen to phosphorus(III) compounds are widely known;[2a] therefore, it seems that this oxygen transfer reaction is the most simple justification for the origin of the oxygen atom bonded to phosphorus in complexes **7** and **8**. Nevertheless, it is well-known[4] that in the decarbonylation reaction of metal carbonyls with **6** 1 mol of carbon dioxide is formed from each 1 mol of *N*-oxide deoxygenated and 2 mol of **6** would be necessary in the reaction of Scheme 1 if the oxygen atom bonded to phosphorus came from the *N*-oxide. The yield obtained using the molar ratio [(Fp)$Ph_2PC{\equiv}CR$][BF_4]/$(CH_3)_3NO$ = 1 (higher than 50% after filtration, extraction, and crystallization: 51%, **7**; 54%, **8**) cannot be achieved by the $(CH_3)_3NO$ molecule because it exceeds its capability of oxygen transfer; thus, water appears as the other most plausible source of oxygen. Moreover, a slight increase in reaction yield was observed (yield ~60%) after the addition of an equimolar amount of aqueous NaOH solution to the reaction mixture.

To examine this hypothesis, we carried out an isotopic labeling study of this reaction using D_2O and $H_2{}^{18}O$. After reaction of **4** with $(CH_3)_3NO{\cdot}D_2O$ the ^1H NMR spectrum of the reaction product showed the aqueous origin of the vinylic hydrogen (integration of vinylic hydrogen shows deuterium labeling of 80%). As expected, when the reaction was carried out using $(CH_3)_3NO{\cdot}2H_2{}^{18}O$ the product did not show any difference in its ^1H or ^{31}P NMR spectra. The water origin of the oxygen atom was definitely established by means of mass spectrometry. The mass spectrum of **7** shows characteristic peaks at *m*/*z* 424 ($M^+ - CO$), 358 ($M^+ - CO - C_5H_6$), 303($M^+ - CO - C_5H_5 - Fe$), 227 ($M^+ - CO - C_5H_5 - Fe - C_6H_4$), and 186 ($M^+ - CO - C_5H_5 - Fe - C_6H_4 - C_2OH$). The labeled ^{18}O complex spectrum shows shifts of +2 units in all the above peaks except for $m/z = 186$ because this fragment does not contain an oxygen atom (Figure 2). For lighter fragments, both labeled and unlabeled spectra are nearly coincident. Furthermore, ^{18}O-labeled and ^{18}O-unlabeled complexes show identical IR spectra in the 4000−400 cm^{-1} region except for the P−O stretching zone.[10]

To the best of our knowledge, this is the first example of the insertion of a water oxygen atom from **6** into an Fe−P bond. Only two examples have been found in the literature in which, by reaction of **6** with metallic clusters, the water oxygen atom is incorporated into the reaction products.[11]

Finally, we should point out the influence of the substituent in the reaction of **1**−**5** with **6**. We observed metallacycle formation only with R = aryl (Scheme 1). This result suggests an intermediate stabilized by charge delocalization on the aryl group and leads us to propose the reaction pathway given in Scheme 2. This tentative reaction pathway is consistent with the reported mechanism for oxidation of metal carbonyls by **6**[4] and with the electrophilic character of the cationic complexes **1**−**5.** Furthermore, there is a strong analogy between the suggested reaction pathway and the well-known mechanism of hydrolysis of quaternary phosphonium salts by aqueous sodium hydroxide[12] (Scheme 3).

Experimental Section

All reactions were performed under nitrogen by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 1710 FT spectrometer. The NMR spectra were recorded by the Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona on a Bruker AM400 instrument. The ^{31}P chemical shifts are reported in ppm upfield from external 85% H_3PO_4. The ^1H and ^{13}C chemical shifts are expressed in ppm upfield from TMS. Mass spectra were obtained on a Hewlett-Packard 5989A spectrometer by a direct introduction probe with ionization energy of 70 eV by Servei d'Anàlisi Química del Departament de Química de la Universitat Autònoma de Barcelona.

$(CH_3)_3NO$, $(CH_3)_3NO{\cdot}2H_2O$, and $H_2{}^{18}O$ (95 atom % ^{18}O) were purchased from Aldrich Chemical Co. The cationic complexes [(Fp)$Ph_2PC{\equiv}CR$][BF_4] were prepared by published procedures.[3] Microanalyses were performed by the Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona. Crystal structure determination was performed by the Servei de Difracció de Raigs X de la Universitat Autònoma de Barcelona.

Synthesis of [CpFe(CO)(η^2(*O*,*C*)-$Ph_2P(O)CH{=}CPh$)] (7) and [CpFe(CO)(η^2(*O*,*C*)-$Ph_2P(O)CH{=}CTol$)] (8). The solid compound **6** (0.10 g, 0.90 mmol) was added to a solution of **4** or **5** (0.50 g of **4** and 0.51 g of **5**, respectively, 0.91 and 0.90 mmol) in dichloromethane (15 mL). The reaction was moni-

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(10) The most remarkable feature is the absence of an intense band at 1127 cm^{-1} and the presence of an intense band at 1040 cm^{-1} (the shift of 87 cm^{-1} in **7** is more than the 42 cm^{-1} predicted for a simple harmonic oscillator). A very similar position (1126 cm^{-1}) has been assigned to the P−O stretch in a related tungsten metallacycle.[6b]

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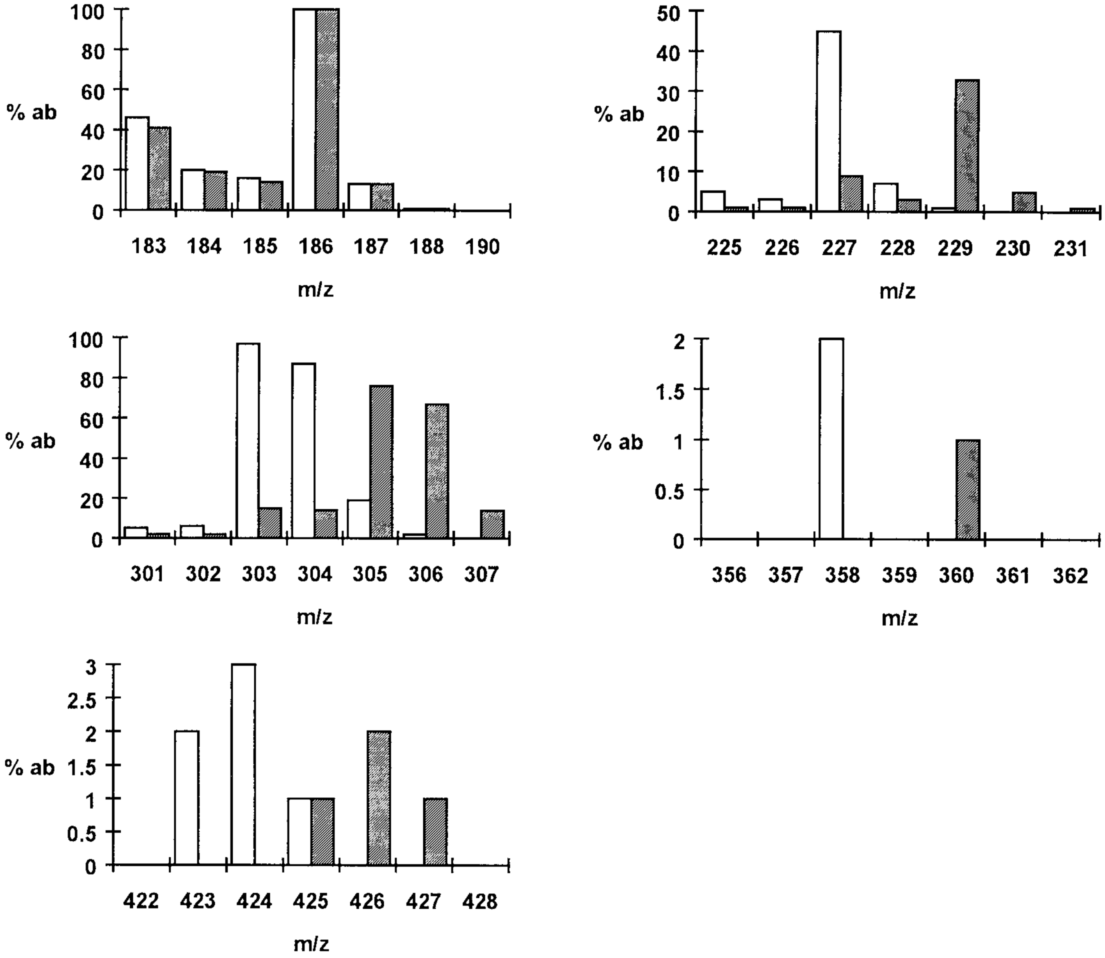
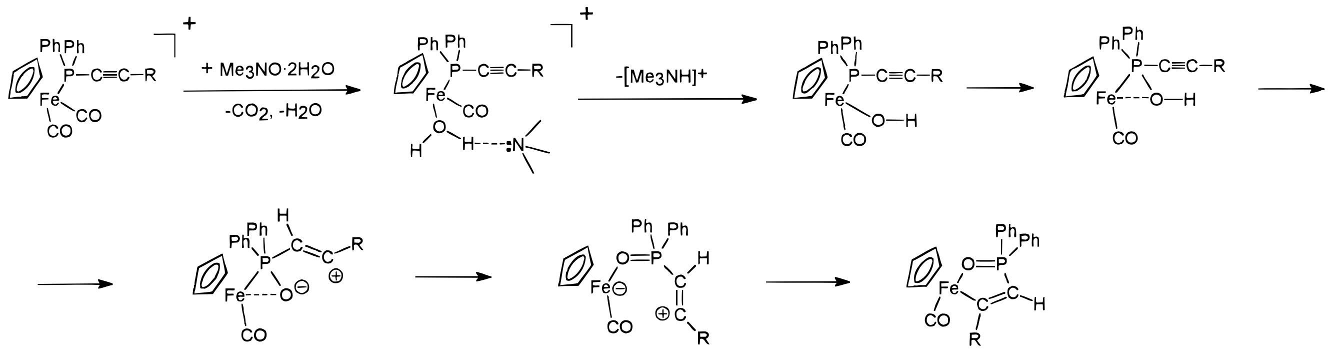
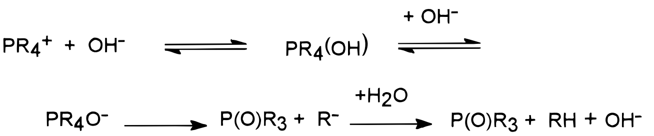


Figure 2. Selected MS regions for the complexes [CpFe(CO)(Ph$_2$P(O)CH=CPh)] (white) and [CpFe(CO)(Ph$_2$P(^{18}O)CH=CPh)] (shaded).

Scheme 2



Scheme 3



tored by IR spectroscopy (ν_{CO} region), and after nearly 1 h of stirring at room temperature, the solution was filtered and evaporated to dryness. The residual solid was extracted with light petroleum (3 × 10 mL), and the resulting solution was evaporated to dryness. The residual product was recrystallized from dichloromethane/methanol at −20 °C. The dark green crystals that separated were collected, washed in methanol, and dried *in vacuo*. Yield: 220 mg (51%) for **7** and 240 mg (54%) for **8**. If NaOH (4 mL of a 0.25 M aqueous solution, 1 mmol) is added to the dichloromethane solution, the light petroleum solution has to be dried with Na$_2$SO$_4$, and the yield increases to ~60%.

The presence of water in complexes **7** and **8** is consistent with the NMR results.

Anal. Calcd. for C$_{26}$H$_{21}$FeO$_2$P•1.5 H$_2$O (**7**): C, 65.16; H, 5.05. Found: C, 65.03; H, 4.71. IR (C$_6$H$_{12}$, cm^{-1}): 1934 (s) (ν_{CO}). IR (KBr, cm^{-1}): 1127 (s) (ν_{PO}). ^{31}P NMR ((CD$_3$)$_2$CO): 72.2. ^{1}H NMR ((CD$_3$)$_2$CO): 4.27 (s, Cp), 6.42 (d, J = 48.0 Hz, HC=), 7.7 (m, Ph). ^{13}C NMR ((CD$_3$)$_2$CO; except phenyl resonances): 82.0 (s, Cp), 118.6 (d, J = 124.2 Hz, PC(H)=), 217.6 (d, J = 14.2 Hz, FeC=), 223.4 (s, CO).

Anal. Calcd for C$_{27}$H$_{23}$FeO$_2$P·1.5H$_2$O (**8**): C, 65.74; H, 5.31. Found: C, 65.58; H, 5.01. IR (C$_6$H$_{12}$, cm^{-1}): 1934 (s) (ν_{CO}). IR (KBr, cm^{-1}): 1131 (s) (ν_{PO}). ^{31}P NMR ((CD$_3$)$_2$CO): 72.2. ^{1}H NMR ((CD$_3$)$_2$CO): 2.28 (s, CH$_3$), 4.29 (s, Cp), 6.42 (d, J = 47.2 Hz, HC=), 7.7 (m, Ph). ^{13}C NMR ((CD$_3$)$_2$CO; except phenyl

Table 1. Crystal Data and Structure Refinement for 8

formula	$C_{27}H_{23}O_2PFe$
fw	466.30
space group	$P2_1/c$
a, Å	9.667(2)
b, Å	11.487(1)
c, Å	20.774(3)
β, deg	91.81(1)
V, Å^3	2305.6(6)
Z	4
D_{calcd}, g cm^{-3}	1.343
μ, cm^{-1}	7.44
$F(000)$	968
λ, Å	0.710 69
T, K	298
θ range, deg	1−25
h,k,l range	−11 to +11, 0−13, 0−24
no. of indep rflns	4049
no. of params	268
goodness of fit on F^2	0.951
R indices ($I > 2\sigma(I)$)	$R(F) = 0.041$, $R_w(F^2) = 0.109$
R indices (all data)	$R(F) = 0.087$, $R_w(F^2) = 0.114$
largest diff peak and hole, e Å^{-3}	+0.35/−0.31

resonances): 21.3 (s, CH_3), 82.4 (s, Cp), 118.3 (d, J = 124.1 Hz, PC(H)═), 217.9 (d, J = 14.8 Hz, FeC═), 223.9 (s, CO).

Isotopic Labeling Studies. The labeled compound $(CH_3)_3NO{\cdot}2D_2O$ was prepared by dissolving anhydrous $(CH_3)_3NO$ (0.15 g, 2.0 mmol) in D_2O (0.1 mL, 5.5 mmols), and the resulting solution was evaporated to dryness. The O-18 hydrated N-oxide $(CH_3)_3NO{\cdot}2H_2{}^{18}O$ was prepared by the same method; anhydrous $(CH_3)_3NO$ (0.10 g, 1.3 mmol) was dissolved in $H_2{}^{18}O$ (0.05 mL, 2.7 mmol), and the resulting solution was evaporated to dryness. The IR spectrum of the O-18 hydrated N-oxide is identical with the unlabeled compound in the stretching (N−O) region (both spectra are indistinguishable between 1500 and 400 cm^{-1}), in agreement with the absence of oxygen scrambling in the labeled compound. White solids were obtained with both procedures.

The complexes [CpFe(CO)($Ph_2P(O)CD$═CPh)] and [CpFe(CO)($Ph_2P(^{18}O)CH$═CPh)] were prepared in accordance with the previously described method, with $(CH_3)_3NO{\cdot}2H_2O$ being replaced by the corresponding labeled compound. Yields were similar to the reported value for the unlabeled complex.

Crystal Structure Determination of 8. Suitable crystals were grown from dichloromethane/methanol. Relevant crystal data and structure refinement are displayed in Table 1, and selected bond distances and angles are given in Table 2. Cell constants were obtained by least-squares refinement on diffractometer angles for 25 automatically centered reflections. Data were measured on a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and an $\omega-2\theta$ scan. Lp and empirical absorption corrections[13] (T_{min} = 0.898, T_{max} = 0.999) were applied. The structure was solved by direct methods (SHELXS-86)[14] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-93).[15] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions with isotropic temperature factors 1.5 (methyl hydrogens) or 1.2 (the rest) times the U_{eq} values of corresponding carbons.

Table 2. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for 8

Fe−Cl	1.728(4)	P−C21	1.755(3)
Fe−C22	1.970(3)	P−C41	1.790(2)
Fe−O2	2.022(2)	P−C31	1.805(3)
Fe−C(Cp)[a]	2.090(4)	C21−C22	1.349(4)
Cl−O1	1.154(4)	C22−C23	1.481(4)
O2−P	1.506(2)		
Cl−Fe−C22	89.41(1)	O2−P−C31	110.5(1)
C1−Fe−O2	99.0(1)	O21−P−C31	112.0(1)
C22−Fe−O2	86.8(1)	C41−P−C31	106.4(1)
O1−C1−Fe	175.8(4)	C22−C21−P	112.7(2)
P−O2−Fe	113.6(1)	C21−C22−C23	119.0(3)
O2−P−C21	107.6(1)	C21−C22−Fe	118.4(2)
O2−P−C41	110.7(1)	C23−C22−Fe	122.6(2)
C21−P−C41	109.7(1)		

[a] Mean value.

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Supporting Information Available: Figures and tables giving the actual mass spectra of complex **7** and the O-18-labeled complex (5 pages). Ordering information is given on any current masthead page. Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre (U.K.) on quoting the depository number 100511.

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